

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

EMISSION SPECTROSCOPY OF CCl_4 AND BCl_3 PLASMAS DURING ALUMINUM ETCHING

By John E. Spencer and Betty Y. Shu
MOS Process Development Laboratory
Texas Instruments Incorporated

P.O. Box 1443 M/S 631, Houston, Texas 77001

and

Texas Instruments Incorporated
P.O. Box 225621 M/S 976, Dallas, Texas 75265

ABSTRACT

Spectroscopy of BCl_3 and CCl_4 plasmas shows major differences that can be related to their etch characteristics. BCl_3 alone etches Al_2O_3 readily, but etches aluminum slowly. Adding Cl_2 reduces its effectiveness at etching Al_2O_3 , but allows a very rapid aluminum etch. The spectra of CCl_4 plasmas do not reveal major differences in chemistry with the addition of Cl_2 . From spectral evidence the main difference between the two gases is that CCl_4 is a much better source of atomic chlorine than is BCl_3 . Plasmas of CCl_4 alone, CCl_4 plus Cl_2 , and BCl_3 plus Cl_2 show a strong band emission at 257 nm due to Cl_2 . This band can obscure the 261 nm band of $AlCl$ that is often used as an endpoint signal. The intensity of this band is very sensitive to the presence of aluminum in the plasma. The Cl_2 signal is quenched after etch initiation, when $AlCl$ emission is detected. As the slice clears and the $AlCl$ emission disappears, the Cl_2 signal returns. The Al atomic emission lines at 394 and 396 nm have no interference and are suggested as better lines for end point detection.

Introduction

Plasma spectroscopy offers an excellent window into the mechanism of plasma etching. This is particularly true when the etch has a large chemical component. In that case the plasma will emit the characteristic spectral emissions of both reactant and product species. This is already widely used in endpoint detection in silicon (1) and aluminum etching (2). This paper will examine the plasma emission spectra toward elucidating etching mechanisms of various gases in aluminum processing.

Two commonly used gases in Al thin film etching are CCl_4 and BCl_3 , either alone or in combination with Cl_2 . Ar or He is usually added as a diluent. These gases show great differences in their spectral characteristics, especially in the region between 250 and 400 nm. Emissions from reactant gas fragments as well as Cl_2 , Al , and $AlCl$ are



ircuit shrunked
llest resist
resist on

observed in this region (3). Atomic Cl can be detected at 726 nm. These spectra can be related to their etching properties. Furthermore, examination of traces of both AlCl and Al emission during etching shows significant differences that should be taken into account in selecting an end point signal.

Experimental

All data reported here were obtained with a load-locked parallel plate plasma reactor with an anodized aluminum interior. Spectra were recorded with a quarter meter monochromator with 2 nm resolution. All plasma conditions were at 1.0 torr with 13.56 MHz excitation.

Results and Discussion

The spectrum of 1% CCl₄ in Ar shows bands due to Cl₂ at 257, 308 nm and CCl at 272-279 nm. No Al or AlCl emission is observed when the plasma is sustained in an empty anodized aluminum etch chamber. The addition of a small amount of Cl₂ equal to the CCl₄ in the plasma causes the CCl emission to be greatly reduced while emissions from Cl₂ and Cl grow in intensity.

The spectrum of 2% BCl₃/Ar in an empty anodized aluminum chamber shows several major differences over the CCl₄ plasma. No Cl₂ emission is seen, and atomic Cl emission is weaker than with CCl₄. BCl emission between 266 and 285 nm is very strong. The band of AlCl at 261 nm is seen with strong intensity, as are strong aluminum lines at 394, 396 nm, and weak aluminum lines at 308, 309 nm. The addition of a small amount of Cl₂ to the plasma removes any emission due to Al species, reduces the BCl emission, and results in strong Cl₂ emission.

BCl₃ is regarded as an excellent etch initiator with a rapid etch rate of native aluminum oxide. The spectral data corroborate this, since the presence of Al and AlCl emission from an anodized aluminum chamber is direct evidence of etching of aluminum oxide. The absence of Al emission from the empty chamber when CCl₄ is used suggests that BCl₃ is a much better aluminum oxide etchant than is CCl₄. This is in contrast to a published report that states that CCl₄ is a faster etchant for aluminum oxide than is BCl₃ (4). Moisture contamination could not have been the reason for this difference since the load locks on the reactor always provided very reproducible etch initiation with both BCl₃ and CCl₄. The addition of Cl₂ to the BCl₃ plasma suppresses Al emission, indicating that oxide etching becomes inefficient in the presence of added Cl₂. However, because of the overlapping of the broad 257 nm band of Cl₂ with the 261 nm band of AlCl, this correlation is not clear. To test this a silicon slice with an aluminum thin film was etched while the plasma spectrum was repetitively scanned

at 726 nm.
es. Furthermore,
ing etching
account in

locked parallel
r. Spectra were
reso-
3.56 MHz exci-

Cl₂ at 257,
is observed
inum etch
to the CCl₄ in
ed while emis-

luminum chamber
No Cl₂ emis-
th CCl₄. BCl₃
and of AlCl₃ at
uminum lines
. The addition
ssion due to Al
ng Cl₂ emission.

ith a rapid etch
oborate this,
dized aluminum
e. The absence
d suggests that
Cl₄. This is in
s a faster etch-
tamination could
load locks on
tiation with
lasma suppresses
fficient in the
oping of the
this correla-
an aluminum thin
vely scanned

between 255 and 265 nm to monitor both Cl₂ and AlCl₃ emission. This is shown in Figure 1. Simultaneously the emission at 395 ± 3 nm was monitored to follow the Al atomic emission lines. This is shown in Figure 2. The atomic emission shows a steep onset and drop off as the slice clears. The 255-265 nm region shows an interesting quenching effect. During the induction period before the penetration of the native oxide film, Cl₂ emission is very strong and no AlCl₃ signal is observed. The appearance of the AlCl₃ signal is accompanied by the decrease and disappearance of the Cl₂ signal. As the slice clears, the process is reversed. This behavior suggests caution in using the 261 nm band of AlCl₃ as an end point for Al etch. The fall of one signal and rise of another overlapping signal could obscure the end point trace.

From the spectral data, BCl₃/Ar is an excellent etch gas for aluminum oxide. However, when aluminum coated slices are etched with BCl₃, the etch is very slow unless Cl₂ is added. However, the disappearance of the Al emission from the empty chamber suggests that the addition of Cl₂ to a BCl₃/Ar plasma reduces the effectiveness of BCl₃ in etching oxide. In both the BCl₃ and CCl₄ plasmas, the addition of Cl₂ suppresses dissociation of the other molecule, causing fewer of the active radicals (either BCl or CCl) to be produced. Adding Cl₂ to BCl₃ apparently nullifies one of the advantages ascribed to BCl₃ plasmas, namely its excellent etch initiation (oxide penetration) characteristics. However, the addition of Cl₂ is necessary to enhance the etch rate of an aluminum film.

The etching characteristics of CCl₄ do not appear to be changed quite so drastically by the addition of Cl₂. CCl₄/Ar alone apparently produces considerable amounts of free chlorine as well as sufficient CCl radicals to penetrate the oxide and initiate etch. Addition of Cl₂ increases the atomic Cl concentration and accelerates the etch. A CCl₄ plasma does not etch the anodized aluminum chamber at a spectroscopically detectable rate.

A particularly interesting feature of the spectra of aluminum etch plasmas is the behavior of the Cl₂ band emission at 257 nm. The Cl₂ emission is highly sensitive to the onset and completion of the etch. This behavior is contrasted to that of the atomic Cl emission line at 726 nm. When the Cl emission was monitored during etching under the same conditions as Figure 1, the Cl signal dropped by about 25% after etch initiation, and rose to its original level as the film cleared. Simple depletion of chlorine species does not account for the loss of the Cl₂ signal.

The 257 nm band of Cl₂ is a known bond-to-bond transition originating above the dissociation energy of the chlorine molecule (5). The upper state is ionic in character and the lower state is covalent. The upper state is efficiently pumped by the discharge. The AlCl₃ band originating at 261 nm provides a non-radiative path for

quenching the excited Cl_2 . Another similar band of Cl_2 occurs at 308 nm. It is readily observed in the absence of aluminum species in the plasma. Like the 257 nm band, it is quenched by the presence of Al species. In this case, the quenching species is probably the Al atom resonance state originating at 308 nm.

The 261 nm band of AlCl is widely reported as a suitable endpoint signal for aluminum etching. However, the behavior of the overlapping 257 nm Cl_2 band suggests caution in its use. The opposing behavior of the two signals can make the endpoint ambiguous. A preferable signal for CCl_4 or BCl_3 plasmas are the Al lines at 394 and 396 nm. No other lines in the region between 390 and 400 nm are detected with either He or Ar diluents. This allows for use of an interference filter to isolate the two lines. As shown in Figure 2, they produce a sharp endpoint under conditions where 261 nm can be ambiguous.

References

1. W.R. Harshbarger, T.A. Miller, P. Norton, and R.A. Porter, Appl. Spectroscopy **31**, 201 (1977).
2. B.J. Curtis and H.J. Brunner, J. Electrochem. Soc., **125**, 829 (1978).
3. R.W.B. Pearse and A.G. Gaydon, The Identification of Molecular Spectra London: Chapman and Hall, 4th edition, 1976.
4. K. Tokunaga, F.C. Redeker, D.A. Danner, and D.W. Hess, J. Electrochem. Soc., **128**, 351 (1982).
5. M. McCusken, "The Rare Gas Excimers," in Excimer Lasers, ed. Ch. K. Rhodes. Berlin: Springer-Verlag, 1979.

Cl_2 occurs at aluminum species in the presence of probably the Al

suitable end-behavior of the use. The ppos-nt ambiguous. A lines at 394 and 400 nm are for use of an own in Figure 2, 261 nm can be

A. Porter, Appl.

ic., 125, 829

in of Molecular 1976.

Hess, J.

Lasers, ed. Ch.

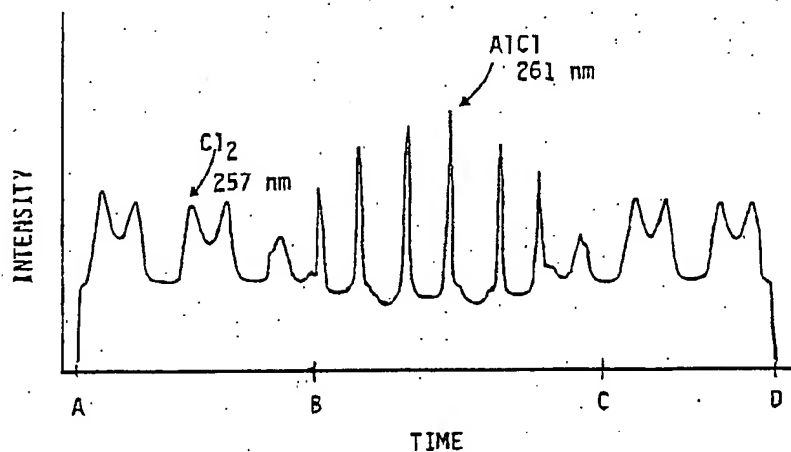


Figure 1.

Repetitive scan during etching an aluminum coated wafer with BCl_3/Ar . The spectrum was repetitively forward and reverse scanned between 255 and 265 nm. The broad band is Cl_2 emission centered at 257 nm and the sharp spike is due to AlCl_3 at 261 nm. During the induction period (A to B) only Cl_2 is observed. During etching (B to C) only AlCl_3 is observed. After the slice clears (C, only Cl_2 emission is observed. RF is turned off at point D.

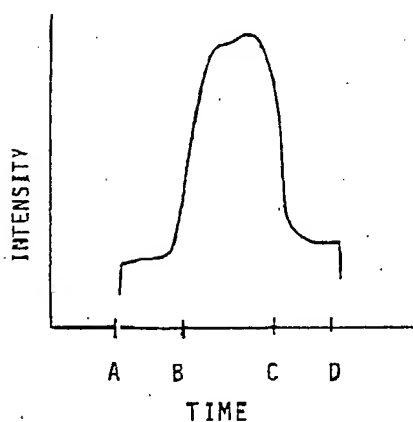


Figure 2.

Trace of the signal generated at 395 nm and recorded simultaneously with the trace shown in Figure 1. Signal was detected through a 5 nm half bandwidth interference filter to detect both aluminum lines at 394 & 396 nm. Time scale is compressed by a factor of 3.5 compared to Figure 1. Points A, B, C, D correspond to RF on, etch initiation, etch termination, and RF off, respectively.

THIS PAGE BLANK (USPTO)